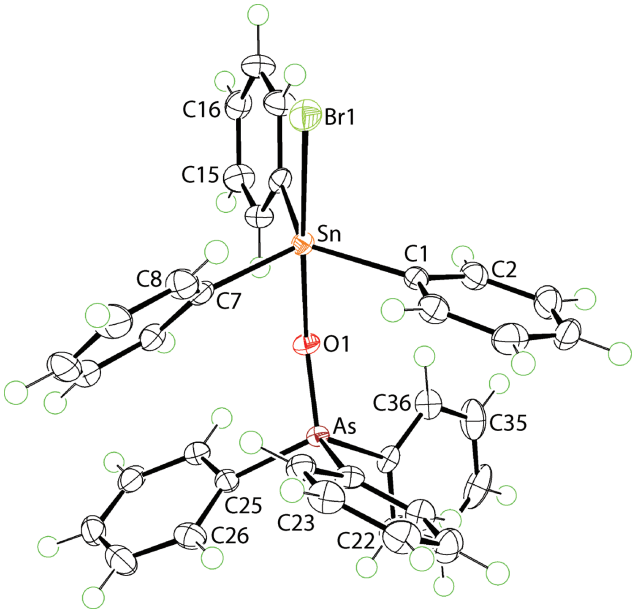
Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink*

Crystal structure of bromido-triphenyl-(triphenylarsine oxide-κ*O*)tin(IV), $C_{36}H_{30}AsBrOSn$



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Abstract

$C_{36}H_{30}AsBrOSn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.8316(1)$ Å, $b = 10.8781(2)$ Å, $c = 14.9388(2)$ Å, $\alpha = 102.367(1)°$, $\beta = 93.369(1)°$, $\gamma = 103.134(1)°$, $V = 1510.07(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0175$, $wR_{ref}(F^2) = 0.0469$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520

Kong Mun Lo and See Mun Lee: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.08 × 0.06 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	9.70 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	35879, 5393, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5331
$N(param)_{refined}$:	361
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

Tetraphenyltin (0.85 g, 2 mmol) and 4-(dimethylamino)pyridine hydrobromide perbromide (Sigma-Aldrich; 0.72 g, 2 mmol) were dissolved in ethanol (50 mL). The resulting mixture was stirred at room temperature until a colourless solution was obtained. Next, triphenylarsine oxide (Sigma Aldrich; 0.64 g, 2 mmol) in ethanol (10 mL) was added to the mixture which was then refluxed for 3 h. After filtration, the filtrate was evaporated slowly until colourless crystals formed. The crystals were filtered, washed with a minimum amount of hexane and air-dried. Yield: 0.88 g (59.1%). **M.pt** (Mel-temp II digital melting point apparatus): 447–449 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1085 (m) ν(C—C), 997 (m) ν(As—O), 476 (w) ν(Sn—O). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me_4Si, $CDCl_3$ solution at 40 °C; ppm): δ 7.47–7.66 (m, 30H, Phenyl-H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 128.0, 129.3, 131.5, 131.9, 132.5, 136.4 (Phenyl—C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Comment

Recently, the X-ray crystal structure determinations of two new triorganoarsine oxide adduct of organotin species were described, namely six-coordinate, *trans*-(4-$MeC_6H_4CH_2)_2SnCl_2(O{=}AsPh_3)_2$ [5] and five-coordinate (4-$MeC_6H_4CH_2)_3SnCl(O{=}AsPh_3)$ [6]. The rest of the known,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Sn	0.78069(2)	0.55247(2)	0.73706(2)	0.01062(5)
As	0.69267(2)	0.21868(2)	0.76382(2)	0.00971(6)
Br1	0.87976(2)	0.75872(2)	0.66552(2)	0.01932(6)
O1	0.69163(14)	0.37567(13)	0.79001(9)	0.0131(3)
C1	0.6651(2)	0.44394(18)	0.60825(13)	0.0128(4)
C2	0.5188(2)	0.4096(2)	0.59939(14)	0.0170(4)
H2	0.470875	0.439276	0.649927	0.020*
C3	0.4420(2)	0.3326(2)	0.51763(15)	0.0223(5)
H3	0.342152	0.311435	0.511968	0.027*
C4	0.5110(3)	0.2870(2)	0.44464(15)	0.0231(5)
H4	0.458781	0.233455	0.388917	0.028*
C5	0.6570(3)	0.3195(2)	0.45267(15)	0.0222(5)
H5	0.704572	0.287004	0.402748	0.027*
C6	0.7335(2)	0.3993(2)	0.53358(14)	0.0174(4)
H6	0.833255	0.423715	0.538001	0.021*
C7	0.9875(2)	0.53195(18)	0.77377(13)	0.0138(4)
C8	1.0990(2)	0.5641(2)	0.72234(15)	0.0181(4)
H8	1.084950	0.598993	0.670421	0.022*
C9	1.2304(2)	0.5454(2)	0.74644(17)	0.0241(5)
H9	1.305319	0.567521	0.710944	0.029*
C10	1.2523(2)	0.4945(2)	0.82198(17)	0.0245(5)
H10	1.342130	0.481936	0.838326	0.029*
C11	1.1424(2)	0.4620(2)	0.87383(15)	0.0207(4)
H11	1.156961	0.426572	0.925439	0.025*
C12	1.0119(2)	0.48123(19)	0.85021(14)	0.0162(4)
H12	0.937707	0.459715	0.886401	0.019*
C13	0.6917(2)	0.65907(19)	0.84714(13)	0.0127(4)
C14	0.6474(2)	0.60513(19)	0.92056(14)	0.0159(4)
H14	0.646868	0.517112	0.918440	0.019*
C15	0.6040(2)	0.6784(2)	0.99664(14)	0.0198(4)
H15	0.574648	0.640148	1.046027	0.024*
C16	0.6034(2)	0.8065(2)	1.00092(14)	0.0181(4)
H16	0.574089	0.856503	1.053098	0.022*
C17	0.6460(2)	0.8614(2)	0.92854(15)	0.0205(4)
H17	0.645558	0.949286	0.930939	0.025*
C18	0.6893(2)	0.7883(2)	0.85240(14)	0.0187(4)
H18	0.717795	0.826951	0.803028	0.022*
C19	0.7680(2)	0.16074(19)	0.65139(13)	0.0133(4)
C20	0.6827(2)	0.0670(2)	0.57993(14)	0.0170(4)
H20	0.588107	0.029310	0.587122	0.020*
C21	0.7374(2)	0.0287(2)	0.49753(14)	0.0208(4)
H21	0.680067	−0.036182	0.448434	0.025*
C22	0.8749(2)	0.0847(2)	0.48676(14)	0.0201(4)
H22	0.911131	0.059244	0.429995	0.024*
C23	0.9601(2)	0.1783(2)	0.55919(15)	0.0190(4)
H23	1.054520	0.216347	0.551712	0.023*
C24	0.9078(2)	0.21616(19)	0.64194(14)	0.0157(4)
H24	0.966066	0.278993	0.691694	0.019*
C25	0.7981(2)	0.18617(18)	0.86439(13)	0.0128(4)
C26	0.9084(2)	0.1262(2)	0.85161(15)	0.0179(4)
H26	0.928468	0.091814	0.791238	0.021*
C27	0.9891(2)	0.1175(2)	0.92865(16)	0.0228(5)
H27	1.066662	0.079195	0.920912	0.027*
C28	0.9568(2)	0.1643(2)	1.01673(16)	0.0224(5)
H28	1.012568	0.158006	1.068909	0.027*
C29	0.8436(2)	0.2201(2)	1.02907(15)	0.0203(4)
H29	0.820044	0.249387	1.089398	0.024*
C30	0.7647(2)	0.23313(19)	0.95272(14)	0.0154(4)
H30	0.688841	0.273633	0.960667	0.018*
C31	0.5021(2)	0.12307(19)	0.75776(13)	0.0125(4)
C32	0.4716(2)	−0.0060(2)	0.76344(14)	0.0175(4)
H32	0.544719	−0.049488	0.766518	0.021*
C33	0.3328(3)	−0.0705(2)	0.76455(15)	0.0250(5)
H33	0.310563	−0.158785	0.768413	0.030*
C34	0.2268(2)	−0.0068(2)	0.76006(15)	0.0272(5)
H34	0.132132	−0.051425	0.761224	0.033*
C35	0.2574(2)	0.1212(2)	0.75388(14)	0.0244(5)
H35	0.183873	0.164171	0.750373	0.029*
C36	0.3961(2)	0.1872(2)	0.75281(14)	0.0173(4)
H36	0.417873	0.275403	0.748731	0.021*

comparatively rare mononuclear species are also five-coordinate, that is, $(4\text{-}ClC_6H_4CH_2)_3SnCl(O{=}AsPh_3)$ [7], $Ph_3SnCl(O{=}AsPh_3)$ [8] and $(4\text{-}ClC_6H_4)_3SnCl(O{=}AsPh_3)$ [8]. In continuation of previous structural studies in this area [5, 6, 8], the crystal and molecular structures of the title triphenylarsine oxide adduct of tri(4-methylbenzyl)tin bromide, $Ph_3SnBr(O{=}AsPh_3)$, (I), are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and features a distorted trigonal bipyramidal geometry with the three phenyl rings occupying equatorial positions, and with the bromido [Sn—Br1 = 2.6983(2) Å] and As-oxido [Sn—O1 = 2.2493(13) Å] atoms occupying axial positions; Br1—Sn—O1 = 177.18(3)°. The Sn atom lies 0.119(1) Å out of the trigonal plane in the direction of the Br1 atom. The Sn—C bond lengths span an experimentally distinct range, that is, from short Sn—C1 = 2.1326(19), Sn—C7 = 2.147(2) to longer Sn—C13 = 2.1514(19) Å. Similarly, there is a disparity in the C—Sn—C angles with the widest angles of C1—Sn—C7 = 120.16(7)° and C1—Sn—C13 = 124.06(7)° involving the C1-phenyl ring which forms the smallest dihedral angle with the C_3 plane, that is, 21.95(7)° and the shortest Sn—C1 bond. The comparable dihedral angles for the C7- and C13-phenyl rings are 57.64(5) and 79.388(7)°, respectively, with the greater dihedral angle correlating with the longest Sn—C13 bond. When the molecule of (I) is viewed down the Sn···As axis, the phenyl rings bound to the Sn and As atoms are close to being staggered. The Sn—O1—As angle is bent, presenting an angle of 136.77(7)°. The C_3O donor set around the As atom is based on a tetrahedron with the range of angles subtended at the As atom being a narrow 106.45(8)° for O1—As—C31 to a wide 115.55(7)° for O1—As—C19, indicating relatively minor distortions from the ideal geometry.

The most closely related literature precedent to (I) is the chlorido analogue, $Ph_3SnCl(O{=}AsPh_3)$, (II) [8]; the structures are not isostructural. As would be expected, very similar coordination geometries are noted. The Cl1—Sn—O1 angles in (II) are 139.3(2) and 139.4(2)° for the two independent molecules comprising the asymmetric unit and are over two degrees wider compared with (I). The As—O bond lengths, that is 1.6709(13) Å in (I), and 1.672(4) and 1.663(4) Å in (II), are equal within experimental errors suggesting little influence exerted by the Sn-bound halide atom upon the mode of coordination of $O{=}AsPh_3$. Such invariance in the As=O bond lengths is consistent with that noted previously for analogous P=O bonds in phosphineoxide adducts of organotin species [9].

In the molecular packing of (I), As-phenyl-C—H···Br contacts [C34—H34···Br1^{i}: H34···Br1^{i} = 2.91 Å, C34···Br1^{i} = 3.752(2) Å with angle at H34 = 149° for symmetry operation (i) $-1+x$, $-1+y$, z] lead to supramolecular chains aproximately parallel to [3 5 −13]. The connections between the chains are of the type phenyl-C—H···π(phenyl). Thus, Sn—phenyl-C—H···π(As-phenyl) [C16—H16···Cg(C31—C36)^{ii}: H16···Cg = 2.75 Å with angle at H16 = 142° and C17—H17···Cg(C24—C30)^{iii}: H17···Cg = 2.91 Å with angle at H17 = 130° for (ii) $1-x$, $1-y$, $2-z$ and (iii) x, $1+y$, z] and As—phenyl-C—H···π(Sn-phenyl) [C29—H29···Cg(C7—C12)^{iv}: H29···Cg = 2.68 Å with angle at H29 = 131° for (iv) $2-x$, $1-y$, $2-z$] are apparent. The layers interdigitate along the c-axis allowing for π-stacking interactions between centrosymmetrically-related Sn-bound phenyl rings [Cg(C1—C6)···Cg(C1—C6)^{v} = 3.9112(13) Å for (v) $1-x$, $1-y$, $1-z$]. It is noted that the phenyl rings are off-set with a slippage of 1.75 Å [10].

The lack of directional interactions in the crystal of (I) is reflected in the analysis of the calculated Hirshfeld surfaces and two-dimensional fingerprint plots (overall and decomposed). The calculations were performed with Crystal Explorer 17 [11] following standard protocols [12]. The specified H···Br contacts leading to the supramolecular chain contribute 7.5% to the overall surface whereas the C···H/H···C contacts, largely corresponding to the C—H···π(phenyl) and π···π interactions, contribute 30.7% of all contacts. Small contributions of 1.5%, due to C···C contacts, and 0.3%, due to C···Br/Br···C contacts, are also noted. However, the most significant contribution, that is, 60.0%, arise from H···H surface contacts.

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